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Assessment of Non-traditional Isotopic Ratios by Mass Spectrometry for Analysis of Nuclear Activities: Annual Report Year 2

S. Biegalski, B.A. Buchholz

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ANNUAL REPORT – YEAR 2

Assessment of Non-traditional Isotopic Ratios by Mass Spectrometry for Analysis of Nuclear Activities

STEVEN BIEGALSKI, PH.D., P.E
THE UNIVERSITY OF TEXAS AT AUSTIN
1 UNIVERSITY STATION, R9000
AUSTIN, TX 78712

BRUCE BUCHHOLZ, PH.D.
CENTER FOR ACCELERATOR MASS SPECTROMETRY
LAWRENCE LIVERMORE NATIONAL LABORATORY
MAIL STOP L-397, P.O. Box 808
7000 EAST AVENUE
LIVERMORE, CA 94551-9900

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Objectives

The objective of this work is to identify isotopic ratios suitable for analysis via mass spectrometry that distinguish between commercial nuclear reactor fuel cycles, fuel cycles for weapons grade plutonium, and products from nuclear weapons explosions. Methods will also be determined to distinguish the above from medical and industrial radionuclide sources. Mass spectrometry systems will be identified that are suitable for field measurement of such isotopes in an expedient manner.

There has been no change in objectives since the initial proposal.

Status of Effort

Significant progress has been made with this project within the past year:

- Isotope production from commercial nuclear fuel cycles and nuclear weapons fuel cycles have been modeled with the ORIGEN and MCNPX codes.
- MCNPX has been utilized to calculate isotopic inventories produced in a short burst fast bare sphere reactor (to approximate the signature of a nuclear weapon).
- Isotopic ratios have been identified that are good for distinguishing between commercial and military fuel cycles as well as between nuclear weapons and commercial nuclear fuel cycles.
- Mass spectrometry systems have been assessed for analysis of the fission products of interest.
- A short-list of forensic ratios have been identified that are well suited for use in portable mass spectrometry systems.

Accomplishments/New Findings

This work investigated isotopic ratios that distinguish nuclear weapons and shortened nuclear fuel cycles from commercial nuclear reactors. The difference between ratio values was determined via Equation 1.

$$R = \frac{\left(\frac{{}^A_Z X\right)_{reactor1}}{\left(\frac{{}^B_Z X\right)_{reactor1}}}{\left(\frac{{}^A_Z X\right)_{reactor2}}{\left(\frac{{}^B_Z X\right)_{reactor2}}} \quad (1)$$

where

- $\left(\frac{{}^A_Z X\right)_{reactor1}$ is the concentration of isotope A produced in a power reactor
- $\left(\frac{{}^B_Z X\right)_{reactor1}$ is the concentration of isotope B produced in a power reactor
- $\left(\frac{{}^A_Z X\right)_{reactor2}$ is the concentration of isotope A produced in a weapon/short burn
- $\left(\frac{{}^B_Z X\right)_{reactor2}$ is the concentration of isotope B produced in a weapon/short burn

Modeling was done using ORNL isotope generation and depletion code ORIGEN-ARP and LANL MCNPX. Three reactor types were modeled within ORIGEN: BWR, PWR, and CANDU. For each reactor type, an appropriate normal burnup length was chosen as well as 5% of a normal length. The short irradiation time is used to account for those fuel cycles focused on ^{239}Pu production rather than nuclear power in a commercial setting. From these tests, all fission products and actinides in the ORIGEN-ARP library were tracked, including meta-stable states, as any field deployable mass spectrometry unit would likely be unable to distinguish the two. From the data acquired

by the ORIGEN simulations, each possible isotopic ratio was computed for each element present in the output. An algorithm was set up to calculate each unique combination of these elements given that the value of the mass was above some threshold limit dictated by the minimum detectable concentration quoted by common mass spectrometry units. In Table 1, the input parameters are given for each reactor type modeled. Considerations must also be taken to exclude any isotopes that may have half-lives that are unacceptable given the time scales needed to acquire a sample in the field. For the purposes of our test, a decay case was included in the ORIGEN simulation that allowed the fuel isotopics to undergo standard decay for a period that would be suitable for field applications.

Table 1 – Parameters for modeling nuclear fuel cycles.

Type	Enrichment	Irradiation Time (days)	Power Level (MW)
BWR	3%	1460	3579
PWR	4%	1650	3411
CANDU	0.711%	900	2180

Other simulations were completed in MCNPX to model the isotope production from a bare sphere fast reactor of high enrichment. While this is a rather simple model, from an isotope creation/depletion standpoint, this is an approximation to what is produced in a nuclear weapon. In MCNPX, isotope tracking was completed for a large set similar to the ORIGEN set using the new predictor-corrector enhanced burnup/depletion (BURN card). Other benefits of using MCNPX for this calculation include the modeling of a fast neutron energy spectrum for the flux given this critical bare isolated sphere

configuration of ^{235}U . This data was compared to normal BWR fuel cycle data obtained from the ORIGEN calculations. For the purposes and limits of mass spectrometry, the values for our ratio metric are expected to show at least two orders of magnitude difference between the various fuel cycle cases.

Results

The R values for all scenarios were analyzed. Table 2 lists the top isotopic ratios to determine the difference between commercial nuclear fuel cycles and nuclear weapon explosions. Ratios were eliminated due to their chemical for (e.g., a gas), their half-life, and yield.

Table 2. Isotopic ratios to distinguish between commercial nuclear fuel cycles and fissile spheres.

				Present in...			A good isotopic indicator at.....				
	Element	Isotope 1	Isotope 2	^{235}U sphere	Pu sphere	^{233}U sphere	1 Day	7 Days	1 Month	1 Year	10 Years
1	Cs	134	135	Y	Y	Y	Y	Y	Y	Y	Y
2	Eu	154	156	Y	Y	Y	Y	Y	Y	Y	N
3	Pm	147	148	Y	Y	Y	N	Y	Y	Y	N
4	Sn	121	123	Y	Y	Y	N	N	Y	Y	Y
5	Sm	146	151	Y	N	Y	Y	Y	Y	Y	Y
6	Cs	134	136	Y	Y	Y	Y	Y	Y	Y	N
7	Pm	148	149	Y	Y	Y	Y	Y	Y	N	N
8	Ag	108	110	N	Y	N	Y	Y	Y	Y	N
9	Ag	110	111	Y	Y	Y	Y	Y	Y	N	N
10	Pm	148	151	Y	Y	Y	Y	Y	Y	N	N
11	Tb	160	161	Y	Y	Y	Y	Y	Y	N	N
12	Eu	154	157	Y	Y	Y	Y	Y	N	N	N
13	Nb	94	97	Y	Y	Y	Y	Y	N	N	N

Notes on each of the isotopic ratios shown in Table 2 are provided below:

- 1) ^{134}Cs ($T_{1/2} = 2.0648\text{y}$) to ^{135}Cs ($T_{1/2} = 2.3\text{e}6\text{y}$)
 - Top choice
 - Present at ratios greater than 5000 for any reactor/bomb combination and from 1 day to 10 years
 - Quantities greater than 10^{-6} g
- 2) ^{154}Eu ($T_{1/2} = 8.593\text{y}$) to ^{156}Eu ($T_{1/2} = 15.19\text{d}$)
 - Eu-156 not present in appreciable quantities at 10 years
 - Otherwise, ^{156}Eu is always greater than 10^{-8} g
 - Ratios greater than 40,000
- 3) ^{147}Pm ($T_{1/2} = 2.6234\text{y}$) to ^{148}Pm ($T_{1/2} = 5.370\text{d}$, or 41.29d for meta state)
 - Very small quantities of ^{148}Pm , especially after 1 year
 - Lower quantities of ^{148}Pm with plutonium bomb
 - Ratio begins at 600 after 1 day, but rises to $\sim 16,000$ at 1 year
- 4) ^{121}Sn ($T_{1/2} = 27.06\text{h}$, or 55y for meta state) to ^{123}Sn ($T_{1/2} = 129.2\text{d}$)
 - Ratio only present at 1 month or later
 - Very small amount of ^{123}Sn at 10 years (on the order of 10^{-10})
 - Only truly viable from 1 month to one year
 - Ratio generally around 1,000
- 5) ^{146}Sm ($T_{1/2} = 1.03 \times 10^8\text{y}$) to ^{151}Sm ($T_{1/2} = 90\text{y}$)
 - For ^{235}U and ^{239}Pu bombs, low quantities of ^{151}Sm (10^{-10} g)
 - For plutonium, low quantities of Sm-146 (10^{-13} g)
 - If detectable, ratios are on the order of 450,000
- 6) ^{134}Cs ($T_{1/2} = 2.0648\text{y}$) to ^{136}Cs ($T_{1/2} = 13.16\text{d}$)
 - ^{136}Cs not present by 10 years, and present in very small quantities at 1 year (10^{-10})
 - At times 1 month or less, both ^{134}Cs and ^{136}Cs are greater than 10^{-8} g
 - Ratios generally greater than 40,000
- 7) ^{148}Pm ($T_{1/2} = 5.370\text{d}$, or 41.29d for meta state) to ^{149}Pm ($T_{1/2} = 53.08\text{h}$)
 - Not present after 1 month
 - Quantities (from 1 day to 1 month) greater than 10^{-8} g
 - Ratios $\sim 1,000,000$
- 8) ^{108}Ag ($T_{1/2} = 2.37\text{ min}$, or 418y meta state) to ^{110}Ag ($T_{1/2} = 24.6\text{s}$, or 249.78d meta state)
 - Ratio best for plutonium bomb
 - Amounts greater than 10^{-8} g for up to 1 year
 - Ratios $\sim 10,000$
- 9) ^{110}Ag ($T_{1/2} = 24.6\text{s}$, or 249.78d meta state) to ^{111}Ag ($T_{1/2} = 7.45\text{d}$)
 - Not present in appreciable quantities after 1 month
 - Quantities greater than 10^{-8} g (10^{-6} for plutonium bomb, and 10^{-10} for U-233 bomb at 1 month)

- Ratios greater than 100,000 (sometimes 10,000,000)
- 10) ^{148}Pm ($T_{1/2} = 5.370\text{d}$, or 41.29d for meta state) to ^{151}Pm ($T_{1/2} = 1.18\text{ d}$)
 - Not present past 1 month
 - Quantities usually greater than 10^{-6} g , never less than 10^{-8} (at 1 month or less)
 - Ratios in the 100,000s, around 300,000
- 11) ^{160}Tb ($T_{1/2} = 72.3\text{d}$) to ^{161}Tb ($T_{1/2} = 6.88\text{d}$)
 - Present at 1 month or less at 10^{-6} g or greater
 - Ratio is heavily dependent on reactor and bomb type (ranges from 3000 to 80,000)
- 12) ^{154}Eu ($T_{1/2} = 8.593\text{y}$) to ^{157}Eu ($T_{1/2} = 15.18\text{h}$)
 - Ratio present only at 1 and 7 days
 - Present with all bomb and reactor types at greater than 10^{-6} g
 - Ratio greater than 1,000,000
- 13) ^{94}Nb ($T_{1/2} = 20,300\text{ y}$) to ^{97}Nb ($T_{1/2} = 72.1\text{ min}$)
 - Ratio present only at 1 and 7 days
 - Quantities greater than 10^{-6} g
 - Ratio $\sim 11,000$ for uranium bombs, ~ 300 for plutonium

Table 3 lists the isotopic ratios that are best utilized to determine the difference between commercial nuclear fuel cycles and short fuel cycles that would be utilized for weapon's grade Pu production. Similar to the list above the total list of isotopes was reduced due to Ratios were eliminated due to their chemical for (e.g., a gas), their half-life, and yield.

Note that there is some overlap between tables 2 and 3 (e.g., $^{146}\text{Sm}/^{151}\text{Sm}$ and

$^{110}\text{Ag}/^{111}\text{Ag}$).

Table 3. Isotopic ratios to determine the difference between commercial nuclear fuel cycles and short fuel cycles that would be utilized for weapon's grade Pu production.

	Element	Isotope 1	Isotope 2	Present in...			A good isotopic indicator at.....			
				BWR	PWR	CANDU	0 Days	1 Month	1 Year	10 Years
1	Sm	146	151	Y	Y	Y	Y	Y	Y	Y
2	Ba	133	140	Y	Y	N	Y	Y	Y	N
3	Pm	145	147	N	N	Y	Y	Y	Y	Y
4	Cd	109	115	Y	Y	N	Y	Y	Y	N
5	Sm	145	151	Y	Y	Y	Y	Y	Y	N
6	La	137	140	Y	Y	N	Y	Y	Y	N
7	Ag	110	111	Y	Y	Y	Y	Y	N	N
8	Pm	145	151	Y	Y	Y	Y	Y	N	N
9	Pm	145	149	Y	Y	Y	Y	Y	N	N

Notes on each of the isotopic ratios shown in Table 3 are provided below:

- 1) ^{146}Sm ($T_{1/2} = 1.03 \times 10^8 \text{ y}$) to ^{151}Sm ($T_{1/2} = 90 \text{ y}$)
 - Top choice
 - Present at ratios from 2000 at no decay to 300 after 10 years
 - Quantities greater than 10^{-6} g
- 2) ^{133}Ba ($T_{1/2} = 10.51 \text{ y}$) to ^{140}Ba ($T_{1/2} = 12.752 \text{ d}$)
 - Not present with the CANDU
 - Quantities greater than 10^{-8} g
 - Not present at 10 years
 - Ratio $\sim 100,000$
- 3) ^{145}Pm ($T_{1/2} = 17.7 \text{ y}$) to ^{147}Pm ($T_{1/2} = 2.6234 \text{ y}$)
 - Only present with the CANDU
 - Quantities greater than 10^{-6} g
 - Present in all time frames
 - Ratio ~ 500
- 4) ^{109}Cd ($T_{1/2} = 462.5 \text{ d}$) to ^{115}Cd ($T_{1/2} = 53.46 \text{ h}$, or 44.6 d for meta state)
 - Not present with the CANDU
 - Quantities greater than 10^{-8} g
 - Not present at 10 years
 - Ratio greater than 6000
- 5) ^{145}Sm ($T_{1/2} = 340 \text{ d}$) to ^{151}Sm ($T_{1/2} = 90 \text{ y}$)
 - Quantities greater than 10^{-8} g
 - Not present at 10 years
 - Ratio greater than 2500

- 6) ^{137}La ($T_{1/2} = 60000\text{y}$) to ^{140}La ($T_{1/2} = 1.6781\text{d}$)
 - Not present with the CANDU
 - Quantities greater than 10^{-8} g
 - Not present at 10 years
 - Ratio ~ 200
- 7) ^{110}Ag ($T_{1/2} = 24.6\text{s}$, or 249.79d for meta state) to ^{111}Ag ($T_{1/2} = 7.45\text{d}$)
 - Only present at 0 days or 1 month
 - Quantities greater than 10^{-3} g (for the above times)
 - Ratio greater than 150
- 8) ^{145}Pm ($T_{1/2} = 17.7\text{y}$) to ^{151}Pm ($T_{1/2} = 28.4\text{h}$)
 - Present only at or before 1 month
 - Quantities greater than 10^{-8} g
 - Ratio around 2000
- 9) ^{145}Pm ($T_{1/2} = 17.7\text{y}$) to ^{149}Pm ($T_{1/2} = 53.08\text{h}$)
 - Present only at or before 1 month
 - Quantities greater than 10^{-8} g
 - Ratio from 150 (PWR) – 2000 (CANDU)

Mass Spectrometry Assessment

In general, the mass spectrometry (MS) literature contains measurements of stable or long-lived isotopes. Most isotopes with half-lives less than 5 years are measured by decay counting techniques. Isotopes with half-lives less than a year are almost exclusively measured by decay counting. Isotopic pairs that retain their significance and do not decay quickly are most attractive for MS analysis because their signatures are not lost by storage. Furthermore, since they are long-lived, decay counting does not work especially well and there is peer-reviewed literature using MS to measure the isotope.

Isotope Pairs for Comparing a Bare Sphere and a Commercial Fuel Cycle

Table 2, above, may be subdivided into three categories of utility or ease of analysis by MS techniques. An isotopic signature that remains over time is desirable if

one is interested in looking at historical samples. If one is not concerned with older samples, more isotope pairs exist, but MS analysis is more difficult to assess. Isotopes with half-lives on the order of days to months are not reported in the MS literature, so it is difficult to predict analytical success.

Among the pairs listed in Table 2, $^{134}\text{Cs}/^{135}\text{Cs}$ is most robust for mass spectrometry applications. It has a significant signature for all three spheres modeled and lasts more than 10 years. There is relatively little literature on the measurement of Cs isotopes using MS. Generally, the fission product ^{137}Cs is measured rather than ^{135}Cs because of its high fission yield and 30 year half-life. Cs readily forms positive ions and is amenable to detection by inductively coupled plasma mass spectrometry (ICPMS), thermal ionization mass spectrometry (TIMS), and resonance ionization mass spectrometry (RIMS). RIMS has better selectivity than TIMS for suppressing stable ^{133}Cs .

$^{146}\text{Sm}/^{151}\text{Sm}$ is also a useful ratio if sufficient material is available. It is significant across all times examined and has a useful signature for both fissile uranium isotopes. Details on MS measurement of this pair are found below in the comparison of fuel cycles. All other isotopic pairs have one at least one member that is too short to be reported in the MS literature. $^{108\text{m}}\text{Ag}/^{110}\text{Ag}$ is the best ratio for the Pu sphere but there is no report of using MS to measure Ag isotopes.

Isotope Pairs for Comparing Fuel Cycle

The isotopic pairs selected for distinguishing long and short fuel cycles in reactors are shown in Table 3. These isotopic pairs are separated into three categories of utility/attractiveness for mass spectrometry analysis. Isotopic pairs that retain their significance over time are most attractive to MS analysis. Furthermore, since they are long-lived, decay counting does not work especially well and there is peer-reviewed literature using mass spectrometry to measure the isotope. Additionally, any pair that is significant regardless of reactor type is more attractive from a detection perspective. Among the isotopic pairs in Table 3, $^{146}\text{Sm}/^{151}\text{Sm}$ is the best pair for mass spectrometry analysis based on these criteria. Thermal ionization mass spectrometry (TIMS) and inductively couple plasma mass spectrometry (ICP-MS) are both used in the literature to measure naturally occurring isotopes of Sm and ^{151}Sm to sub-part per million concentrations, but there are no reported measurements of ^{146}Sm with these methods. Modeling indicates that ^{146}Sm concentrations will be significantly lower, probably below the range of ICP-MS. TIMS may be capable of measuring ^{146}Sm . It typically has better precision than ICP-MS, but its dynamic range is more limited and sample preparation is difficult. There is no system currently available that reports measurements of the expected $^{146}\text{Sm}/^{151}\text{Sm}$ ratios ($10^{-9} - 10^{-6}$).

The second tier of isotopic pairs in Table 3 fail to meet one of the criteria for the most attractive pair. $^{145}\text{Pm}/^{147}\text{Pm}$ remains a viable signature pair from production through 10 years but is only produced by the CANDU reactor. Since promethium has no

stable isotopes, there is very little literature on mass spectrometry methods for measurement of Pm. ICP-MS has been used in a couple instances to measure ^{147}Pm . Another samarium pair, $^{145}\text{Sm}/^{151}\text{Sm}$, remains viable for about 5 years. The relatively short half-life of ^{145}Sm (340 d) results in loss of signal. Also, there were no reports of mass spectrometry measurement of ^{145}Sm .

All other pairs in Table 3 have one or both members that are too short for reports of mass spectrometry data in the literature.

Personnel Supported

The University of Texas at Austin

Faculty:	Steven Biegalski
Graduate Students:	Jordan Weaver Drew Masada Sarah Williams
Undergraduate Students:	Thomas Saller Frederuck Tuthill

Lawrence Livermore National Laboratory

Scientific Staff:	Bruce Buchholz
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Publications

1. C.J. Weaver, S.R.F. Biegalski, B.A. Buchholz, “ Assessment of Non-Traditional Isotopic Ratios by Mass Spectrometry for Analysis of Nuclear Activities,” *Journal of Radioanalytical and Nuclear Chemistry* (2009), DOI 10.1007/s10967-009-0289-y.
2. B. A. Buchholz, S. R. Biegalski, S. M. Whitney, S. J. Tumey, C. J. Weaver, “The Basis for Developing Samarium AMS for Fuel Cycle Analysis,” submitted to *Nuclear Instruments and Methods B*, (2009).

Interactions/Transitions

Participation in the following meetings/conferences:

1. 11th International Conference on Accelerator Mass Spectrometry (AMS-11), Sep 14-19, 2008, Rome, Italy.
2. DTRA Basic Research Technical Review, Nov. 3-14, 2008, Springfield, VA.
3. 8th Methods and Applications of Radioanalytical Chemistry, April 5-9, 2009, Kona, HI.

New discoveries, inventions, or patent disclosures

No new discoveries, inventions, or patent disclosures.

Honors/Awards:

No honors, degrees, or awards received during the grant/contract period.

Auspices Statement:

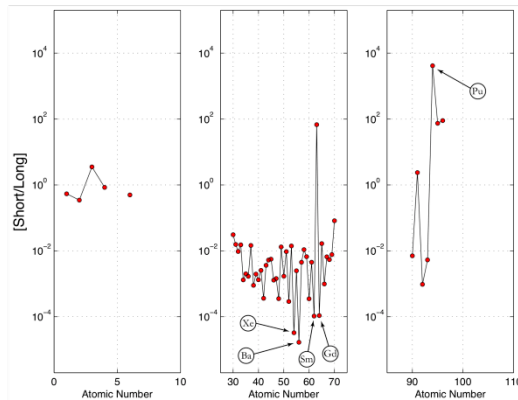
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Quad Chart

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Assessment of Non-traditional Isotopic Ratios by Mass Spectrometry for Analysis of Nuclear Activities, S.R. Biegalski, The University of Texas at Austin, HDTRA1-08-1-0032



•Identify isotope ratio signature needles in the fission product haystacks and describe how to measure them in the field.

Description: Our objective is to identify isotopic ratios suitable for analysis by mass spectrometry (MS) that distinguish between nuclear reactor fuel cycles and products from nuclear weapons explosions. MS systems capable of rapid field measurement will be identified.

Key deliverables:

- International conference paper on the identification of useable forensic signatures.
- International conference paper on mass spectrometry applications for identified forensic signatures.
- Design study paper on optimization of portable mass spectrometry systems for nuclear forensics.

Objectives/Metrics: . Candidate mass spectrometry techniques and systems will be identified and evaluated. The best isotopic ratios for forensic applications to suitable mass spectrometry techniques.

Performer: Steven Biegalski, The University of Texas
Bruce Buchholz, Lawrence Livermore National Laboratory

Status: An initial database of forensic signatures has been developed. The database is currently being refined based on the capabilities of mass spectrometry systems.

Accomplishments:

- Presented paper at AMS 11 conference (2009).
- Presented paper at MARC VIII conference (2009).

Funding Profile:

- 2008-2009 (\$214k) 2009-2010 (\$204k)

Key Milestones:

- Identify isotope ratio signatures for reactor fuel cycles and weapons (2008)
- Assess MS techniques best suited to distinguish signatures (2008-09)
- Determine MS specifications for field deployment (2009)

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